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SPECTROSCOPIC STUDIES OF ORGANOPHOSPHORUS COMPOUNDS Part VII. IR Spectra of Alkyltriphenylphosphonium Compounds*

M. ARSHAD A. BEG and SAMIUZZAMAN

PCSIR Laboratories, Karachi 39

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Abstract. A detailed study of the IR spectra of triphenylphosphine and alkyltriphenylphosphonium iodides and bromides having methyl, *n*-propyl or *n*-butyl as the alkyl group is reported for the 4000–250 cm^{-1} region. Integrated intensity of a number of bands besides the X-sensitive ones shows that the changes in intensity are related to quaternization in the case of the k, m, o, c and q, and to the length of the alkyl chain for n, a, b, d and p. A characteristic feature of the spectra is the splitting of the band in the 750 cm^{-1} region corresponding to the C—H out-of-plane bending. The changes in intensity and splitting of the bands are both interpreted on the basis of induced polarization whereby the formal positive charge on the phosphorus atom creates a polarity in the ring by attracting their π -electron density. The positive inductive effect of the alkyl group is responsible for the increase in the polarity and hence a dependence of the intensity is observed on the alkyl chain-length. The amount of splitting and the intensity of mode n is also found related to the bulk of the alkyl group. The intensity of the P—C (aliphatic) absorption, however, decreases with chain-length. The X-sensitive modes q, y, t and u shift their positions on quaternization of the phosphine.

For the phosphonium bromides the intensity enhancement is at least three times that of the iodides. There is a further shift in the band position and splitting is more pronounced. The P—C stretching frequency is shifted to slightly lower frequencies from $780 \pm 10 \text{ cm}^{-1}$ in the iodides to 765 ± 5 in the bromides.

In our earlier papers¹⁻⁵ we have sought a correlation of the structure of the aryl onium compounds with their spectra. It has been pointed out that the shapes and intensity of the bands have a characteristic pattern. This generalization has been found to be valid in the case of the phosphonium,¹ arsonium,^{2,3} selenonium⁴ and iodonium⁵ compounds. From a general survey of the arylphosphines and arsines and their onium compounds it is found that the three bond angles in the trivalent derivatives are not equal.⁶⁻⁸ The aromatic rings are capable of rotation and make different angles with respect to one another. The rings in quadruply connected compounds tend to acquire a propeller shaped structure which may be further modified with changes in the substituents on the central atom.⁹ Any change in the structure brings about a lowering of symmetry leading to a change in the pattern of the band shapes and in an alteration in the intensity. In order to study the effect of these variations we now report the spectra of the alkyltriphenylphosphonium compounds, where the chain-length of the alkyl groups is increasing from methyl to *n*-butyl. We have also studied the effect of changes of the anion and for this purpose the spectra of the iodides and bromides have been recorded.

The spectra of some triphenylphosphonium compounds have been reported previously.¹⁰⁻¹³ Kross

and Fassel¹⁰ have related the position of the 1090 cm^{-1} band with the electronegativity of the central atom. The band at 1100–1120 cm^{-1} in the phosphonium compounds has been suggested by Witchard and Griffin¹¹ to be characteristic of quaternization. Deacon and Jones¹² and Deacon and Green¹³ have studied the spectra of the methyl and ethyltriphenylphosphonium compounds and their halomercurates and have also made assignment of the absorption bands. Their results are at the most semiquantitative and do not show any differences among charged and neutral substituents on the benzene ring—a fact emphasized by Katritzky. The latter author has studied¹⁴ the effect of different substituents by comparing the integrated intensity of the band at 1600 cm^{-1} . We, however, find that the measurement of the integrated intensity of all the fundamental bands not only sorts out the differences among the charged and neutral species but also shows that other bands besides the X-sensitive modes are susceptible to changes in the length of the alkyl chain and of the anion and greater differences are noted for those bearing a charge than for neutral ones. The present study is thus a quantitative approach in terms of changes in intensity, splitting of bands and related phenomena.

Experimental

Phosphine and phosphonium iodides were prepared by the methods described earlier.¹ The bromides

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were obtained by sealed-tube reactions between equivalent amounts of the phosphine and the respective alkyl bromide. The product was obtained by heating the tube for 48 hr at 110°C. The m.ps. and other analytical data are given in Table 3. The spectra were recorded on Beckman IR-10 spectrophotometer using KBr-pellet through the courtesy of Prof. H.C. Clark, Department of Chemistry, University of Western Ontario, London, Canada. The pellet was very carefully prepared in triplicate and selected on the basis of similarity of results with each other. The integrated intensity was calculated, using the following equation..

$$A = \frac{\nu_{\frac{1}{2}} \times \log I_0/I \times K}{C \times l}$$

Where $\nu_{\frac{1}{2}}$ is half hand width; I_0/I , optical density; K , a constant; C , molar concentration and l is cell length.

Results

The spectra of the alkyltriphenylphosphonium compounds resemble those of the monosubstituted benzenes for which Whiffen has given all the fundamental and combination bands.¹⁵ We have, therefore, adopted his notations. The spectra of triphenylphosphine and the alkyltriphenylphosphonium halides are recorded in Tables 1 and 2 which include the integrated intensity data and the assignment of bands. For the purpose of this study the spectra are divided into four regions: (1) 1600–1300 cm^{-1} , (2) 1300–950 cm^{-1} , (3) 950–650 cm^{-1} and (4) 650–250 cm^{-1} . These

regions pertain to certain sets of aromatic vibrations like the $\nu\text{C}-\text{C}$, $\beta\text{C}-\text{H}$, $\gamma\text{C}-\text{H}$ and the skeletal and X-sensitive vibrations respectively.

The general observation which is immediately apparent from Table 1–3 is that excepting a few modes like m , p and v where the intensity falls from the phosphine to methyltriphenylphosphonium iodide and rises again with chain-length, all the other absorptions have higher intensity compared with the former. These changes can, therefore, be explained on the basis of (1) a lack of resonance interaction due to the absence of lone-pair electrons in the phosphonium compounds and (2) increase in chain-length and a consequent increase in the positive inductive effect.

Discussion

In the previous publications¹⁻³ it has been shown that mode n is highly intensified in the phosphonium and arsonium compounds and splitting in the region 745 cm^{-1} is observed. On the basis of this pattern of absorption, it was concluded that this phenomenon is related to the orientation of the rings in space in the lattice of the phosphonium compounds. The results were supported by the X-ray structural studies of these compounds.^{6,7} The integrated intensity data obtained here reveal that besides the above systematic pattern of absorption there is also an enhancement in intensity of nearly all the modes from the phosphine to onium compounds, except mode m which is always strong in phosphine and weak in the phosphonium compounds. The apparent change in structure from phosphine to phosphonium compounds is the presence of a formal positive charge on the

TABLE 1. IR ABSORPTIONS AND APPARENT INTEGRATED INTENSITIES OF TRIPHENYLPHOSPHINE AND ALKYLTRIPHENYLPHOSPHONIUM IODIDES.

Ph ₃ P		MePh ₃ PI		EtPh ₃ PI		n-PrPh ₃ PI		n-ButPh ₃ PI		Assignment
cm ⁻¹	A	cm ⁻¹	A	cm ⁻¹	A	cm ⁻¹	A	cm ⁻¹	A	
1580	126	1587	216	1588	321	1580	327	1590	583	$\nu(\text{C}-\text{C})$ mode k & l
1470	339	1485	133	1485	276	1482	580	1487	678	$\nu(\text{C}-\text{C})$ mode m
1430	463	1435	1051	1435	1091	1430	851	1435	944	$\nu(\text{C}-\text{C})$ mode n
1325	88	1320	97	1320	351	1315	748	1320	622	$\nu(\text{C}-\text{C})$ mode o
1270	129	—	—	1275	22	—	—	—	—	$\beta(\text{C}-\text{H})$ mode e
1175	59	—	—	1190	0	1190	202	1184	281	$\beta(\text{C}-\text{H})$ mode a
1155	53	—	—	1165	54	1160	484	1165	555	$\beta(\text{C}-\text{H})$ mode e
1090	229	1112	2036	1110	2320	1115	2019	1115	1944	X-sens mode q
1070	254	1075	705	1080	740	1080	756	1075	833	$\beta(\text{C}-\text{H})$ mode d
1025	158	—	—	1020	175	1030	105	—	—	$\beta(\text{C}-\text{H})$ mode b
998	154	1000	131	1000	395	1000	458	1000	616	ring mode p
912	47	910	1971	—	—	900	279	910	200	$\gamma(\text{C}-\text{H})$ mode i
850	17	—	—	—	—	840	313	800	350	$\gamma(\text{C}-\text{H})$ mode g
—	—	793	828	785	527	790	447	—	—	$\nu(\text{P}-\text{C})$ nky
—	—	760	sh	750	sh	750	1745	755	2762	$\gamma(\text{C}-\text{H})$ mode f
745	1200	750	1561	740	2509	738	784	745	2762	
—	—	720	1018	725	1463	723	722	728	7037	
692	1995	690	1980	690	1505	690	1762	695	2129	$\phi(\text{C}-\text{C})$ mode v
625	65	—	—	—	—	—	—	—	—	$\phi(\text{C}-\text{C})$ mode s
545	—	—	—	530	1840	530	969	538	1277	
515	466	508	1745	510	1192	490	550	500	1555	Combination t & x
492	745	493	856	490	640	490	838	—	—	X-sens mode y
—	—	450	184	455	477	458	137	465	337	
432	66	—	—	440	177	435	120	430	188	X-sens mode t
422	64	425	vwv	—	—	415	107	420	163	
—	—	—	—	—	—	—	—	410	133	X-sens mode u
400	43	380	42	390	753	400	77	400	191	
—	—	—	—	—	—	—	—	390	126	$\phi(\text{C}-\text{C})$ mode w

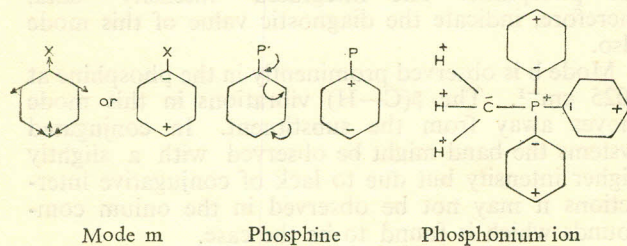
TABLE 2. IR ABSORPTIONS AND INTEGRATED INTENSITIES OF ALKYLTRIPHENYLPHOSPHONIUM BROMIDES.

EtPh ₃ PBr		<i>n</i> -PrPh ₃ PBr		Assignment
cm ⁻¹	A	cm ⁻¹	A	
1584	1498	1585	1332	v(C—C) mode k
1484	1201	1485	1325	v(C—C) mode m
1440	1468	1440	1584	v(C—C) mode n
1330	2442	1330	1572	v(C—C) mode o
1269	747	1250	792	β(C—C) mode e
1195	1070			β(C—H) mode a
1165	1087	1165	955	β(C—H) mode c
1115	6440	1115	3114	X-sens mode q
1085	1133	1082	1914	β(C—H) mode d
1025	1030	1035	990	β(C—H) mode b
1000	1389	1000	752	Ring breath mode p
			847	γ(C—H) mode g
765	1225	766	2796	
760	1918	760	1607	γ(C—H) mode f
740	1949	740	1118	
728	1200	725	1133	
694	2074	700	2551	φ(C—C) mode v

TABLE 3

Compound	M.p.(°C)	C (%)		H (%)	
		Cal	Found	Cal	Found
MePh ₃ PI	165	56.43	56.24	4.45	5.02
EtPh ₃ PI	140	57.43	57.15	4.78	4.72
<i>n</i> -PrPh ₃ PI	190	58.33	58.01	5.09	5.03
<i>n</i> ButPh ₃ PI	210	59.19	59.00	5.38	5.05
EtPh ₃ PBr	205	64.69	64.58	5.39	5.40
<i>n</i> -PrPh ₃ PBr	230	65.45	65.41	5.71	5.02

phosphorus atom instead of a lone-pair. Thus it can be concluded that the enhancement in integrated intensity is related to the formal positive charge on the central atom. The lone-pair would only repel the electron cloud of the ring which may result in lowering the symmetry from C_{3v} to C_s giving rise to nonequivalent rings and in fact the high resolution instruments¹³ and spectra of melt¹⁶ of triphenylphosphine give split bands in the 745 cm⁻¹ region. The vibrations would not be affected very much in the presence of a lone-pair, while the presence of a formal positive charge on the central atom would attract the π-electron density of the rings and polarize the same thus creating increasing disturbances in the ring as compared with the lone-pair. The polarization of the ring would bring about an increase in the transition dipole resulting in an enhancement in the intensity of absorption. Induced polarization also explains the intensification of mode m in phosphine. During vibration corresponding to mode m the charge density is moved slightly towards the substituent and



creates a polarity opposite to that obtained under the influence of a formal positive charge in the phosphonium compounds. Thus mode m has a high intensity in the phosphine than in the phosphonium compounds.

If it is true that an increase in the formal positive charge would increase the intensity of the absorption, the effect should be further felt through a change in the anion such as the bromides and chlorides. The bromide ion being more electronegative polarizes the electron density on the phosphorus atom more and thus the observed intensity of the band is greater than for the iodides. The tetrahalocobaltate ion, to be discussed later, being still more electronegative, further increases the intensity and in this case there is a ten-fold increase in intensity compared with the phosphine. A regionwise detailed account of the spectra is given below for the iodides and the bromides.

1600–1300 cm⁻¹ Region. The C—C skeletal modes, k, l, m, n and o, and C—H alkyl deformation modes are expected to absorb in this region. The following characteristic features have been observed in the spectra: (1) the absorptions for the phosphine are less intense than for the phosphonium compounds excepting mode m where the phosphine absorption is strong, (2) in the phosphonium compounds the intensity increases regularly with increasing chain-length of the alkyl group, and (3) of all the absorptions n mode is very intense followed by one due to m. Mode l is not resolved while o is very weak.

An increase in the intensity of the various modes in the phosphine than the phosphonium compounds may be related to the much greater changes in the dipole of the ion than in the phosphine itself. In analogy with the triphenylmethyl cation,¹⁷ it can be said that the changes in the ring shape during these vibrations cause the net positive charge on the ion to move from one type of location to another across the ring system. This point of view is also supported by the UV spectra of triphenylphosphine where appearance of a structureless band at 260 mμ is due to the conjugation of the phenyl group through the phosphorus atom which is altered in the case of phosphonium compounds to the extent depending on the amount of delocalization of the charge.¹⁸ It is likely that the absorption for the phosphonium compounds are due to the delocalization of the positive charge under induced polarization leading to higher absorptions for the phosphonium compounds than for the phosphine.

Although it is known that an increase in the molecular weight in the homologous series would tend to lower the intensity of the absorption¹⁹ two factors besides molecular weight are important: one is the orientation in the rings and the other is the directing influence of the substituents which in the present case are phosphorus with a lone-pair and charged phosphorus with an alkyl group. Thus a gradual increase in the intensity of the various modes from methyltriphenylphosphonium to *n*-butyltriphenylphosphonium iodide may be attributed to the orientations in that ring so as to interact increasingly as the alkyl group becomes more and more bulky.

In the spectra of the triphenylphosphine and its alkylphosphonium compounds the absorptions due to k and l modes follow the same pattern as the

monosubstituted benzenes. In the phosphine mode *m* is stronger than in the methyltriphenyl and ethyltriphenylphosphonium iodides. The same trend is found in the case of the corresponding triphenylarsonium compounds and may be due to the movement of charge cloud towards the substituent atom, resulting in greater dipole changes for this mode of vibration.

The intensity of the *n* mode which absorbs near 1430 cm^{-1} is very high as compared with the other modes. It is about eight times higher than *m* mode in case of methyltriphenylphosphonium and five times in ethyltriphenylphosphonium iodide. The sequence of increasing intensity is: $\text{Ph}_3\text{P} < \text{MePh}_3\text{PI} < \text{EtPh}_3\text{PI} < n\text{-PrPh}_3\text{PI} < n\text{-ButPh}_3\text{PI}$.

Incidentally this mode also absorbs strongly in all monosubstituted benzenes but the intensity is comparable with the other modes in this region. A tremendous increase in the intensity in the case of phosphine and phosphonium compounds has some sort of relation with a strained structure so as to orientate the ring either out-of-plane with respect to the others or to twist them like propeller blades. A similar effect is also noted in the case of the selenonium compounds⁴ and diphenylarsenic chloride.²⁰ These compounds have at least one ring rotated out-of-plane with respect to the other.

Mode *o* absorbs only weakly near $1322 \pm 3\text{ cm}^{-1}$ and follows the same trend with the intensity increasing with chain-length. The sequence is $\text{Ph}_3\text{P} < \text{MePh}_3\text{PI} < \text{EtPh}_3\text{PI} < n\text{-But Ph}_3\text{PI} < n\text{-PrPh}_3\text{PI}$

It will be noted that the intensity variation is most sensitive with mode *k* and *m* but it is not so neat in other vibrations. Mode *o* is rather peculiar in that the intensity falls from phosphine to methyltriphenylphosphonium but thereafter increases regularly.

1300–950 cm^{-1} Region. In this region five C—H deformation modes *a*, *b*, *c*, *d* and *e*, one ring breathing mode *p* and one X-sensitive mode *q* occur. The characteristic features observed in this region of the spectrum are as follows:

1. Mode *b* is quite intense in the phosphine and is only observed in ethyltriphenyl- and *n*-butyltriphenylphosphonium iodides.

2. Ring breathing mode *p* is stronger and the intensity increase is quite regular in the series.

3. Absorption due to mode *q* is the most intense in the onium compounds and is quite weak in the phosphine. The intensity for this vibration decreases with the chain-length.

4. The observed shifts in mode *q* from triphenylphosphine compared with triphenylarsine are of 36 cm^{-1} while in the corresponding phosphonium compounds compared with the arsoniums these are of the order of 20 cm^{-1} to the higher frequencies.

5. Modes *a*, *e* and *c* absorb very weakly.

A weak band at 1270 cm^{-1} is assigned to mode *e* in triphenylphosphine. A very weak band at 1274 cm^{-1} in ethyltriphenylphosphonium iodide has been assigned by Deacon *et al.*¹² to CH_2 twisting and wagging. A band at 1275 cm^{-1} has also been observed here in the spectra of ethyltriphenylphosphonium iodide. Since this band is observed in all the phenyl arsenic compounds² and is not observed in the *n*-butyl

derivatives of phosphorus, assignment of this band to mode *e* is preferable.

The absorption due to mode *a* is also very weak and is found at 1175 cm^{-1} in triphenylphosphine, at 1190 cm^{-1} in ethyltriphenyl and *n*-propyl triphenylphosphonium and at 1184 cm^{-1} in *n*-butyltriphenylphosphonium iodide. It is absent from the spectrum of methyltriphenylphosphonium iodide. The increase in intensity with chain-length indicates slight interaction of the alkyl group with the ring π -electrons. Revitt and Sowerby²⁰ have observed this band in the spectra of phenyl dichloroarsine and diphenyl chloroarsine at $1181 \pm 2\text{ cm}^{-1}$ as a weak to medium intensity band, while the same occurs at 1179 cm^{-1} in triphenylphosphine,²¹ at 1188 cm^{-1} in triphenylarsine and at 1183 cm^{-1} in arsonium compounds.²² This mode absorbs weakly and is also a weak band in diphenylselenium dichloride and triphenylselenonium chloride.⁴ A band of similar intensity is observed at 1155 cm^{-1} in the phosphine and at 1165 cm^{-1} in all the alkyltriphenylphosphonium iodide where it is not observed. It seems that this vibration which is assigned to mode *c* is shifted to higher frequencies from the phosphine to the phosphonium compounds. A similar behaviour is also observed in the corresponding arsonium compounds. This mode may also be diagnostic for quaternization of phosphorus and arsenic and the shift must be related to the change in hybridization of the phosphorus atom.

Mode *q* absorbs weakly at 1090 cm^{-1} in triphenylphosphine while in all the onium compounds it absorbs at $1110\text{--}1115\text{ cm}^{-1}$ and is very strong. In the case of arsine it has already been suggested to be due to changes in hybridization. According to Kross and Fassel¹⁰ this band moves to higher energies as the electronegativity of the substituent increases. That this shift is due to the change in hybridization is also supported by the occurrence of this band at 1074 cm^{-1} in triphenylarsine, at 1073 cm^{-1} in the spectra of triphenylarsine dichloride, diphenylarsine trichloride, triphenylarsine dibromide and at 1074 cm^{-1} in phenylarsine tetrachloride.²⁰

Mode *d* which absorbs at $1080 \pm 10\text{ cm}^{-1}$ is resolved only in triphenylphosphine, in other compounds it occurs as a weak shoulder.²¹

Deacon and Jones have assigned a shoulder occurring in triphenylphosphine and phosphonium compounds at 1066 cm^{-1} to C—H in plane deformation mode *d*. This band has been shown to be of lower intensity in a strained structure.⁴ Judging from the mode of vibration, its occurrence only in triphenylphosphine and as a weak shoulder in the onium compounds suggests either a lack of conjugative interaction in the phosphonium compounds or that the structure is under considerable strain compared with the phosphine. The integrated intensity data, therefore, indicate the diagnostic value of this mode also.

Mode *b* is observed prominently in the phosphine at 1025 cm^{-1} . The $\beta(\text{C—H})$ vibrations in this mode moves away from the substituent. In conjugated systems the band might be observed with a slightly higher intensity but due to lack of conjugative interactions it may not be observed in the onium compounds which is found to be the case.

The ring breathing mode *p* absorbs strongly near 1000 cm^{-1} in all the phosphonium compounds and the phosphine. In phosphonium compounds the intensity increases with the alkyl chain in the sequence $\text{Ph}_3\text{P} < \text{MePh}_3\text{PI} < \text{EtPh}_3\text{PI} < n\text{-PrPh}_3\text{PI} < n\text{-ButPh}_3\text{PI}$. This shows that there is a neighbouring group contribution to the electron density of the ring.

The various vibrations noted in this region bring forward at least two modes viz: *q* and *c* which are sensitive to quarternization while modes *a*, *b*, *d* and *p* are sensitive to increases in the length of the alkyl chain.

950–650 cm^{-1} Region. The absorptions related to the present series of compounds occur at $650\text{--}750\text{ cm}^{-1}$ (P—C stretching), $698\text{--}779\text{ cm}^{-1}$ (ring deformation mode), 722 cm^{-1} (CH_2 rocking), 894 cm^{-1} (CH_3 rocking) and $937\text{--}71\text{ cm}^{-1}$ ($\gamma(\text{C—H})$). The main features regarding the spectra are: (1) the intensity of P—C stretching frequency decreases with the chain; (2) phosphine has one strong band at 745 cm^{-1} which is split in all the phosphonium compounds into three bands; and (3) the splitting becomes more and more prominent as the chain-length increases from methyl to *n*-propyl. For the *n*-butyl analogue it is not well-resolved.

The P—C stretching frequency absorbs between $750\text{--}650\text{ cm}^{-1}$.²³ In alkyltriphenylphosphonium compounds it is observed near $785\text{--}800\text{ cm}^{-1}$. The intensity of the absorption decreases with increasing chain-length which is expected within the homologous series, since an increase in molecular weight would tend to lower the intensity of absorption.¹⁹

All the monosubstituted benzenes have a characteristic band at 742 cm^{-1} due to C—H out-of-plane bending vibration mode *f*. A strong single band has been observed during this study for the triphenylphosphine at 745 cm^{-1} . Sheldon and Tyres¹⁸ have recorded this band at 742 cm^{-1} . Deacon and Green¹³ on the other hand have reported three bands occurring at 754 , 746 and 741 cm^{-1} while Steger and Stopperka¹⁶ have recorded three bands at 752 , 746 and 726 cm^{-1} .

Since triphenylphosphine is expected to be a symmetrical molecule with symmetry C_{3v} it is possible that the single absorption at 742 cm^{-1} is due to the degeneracy of the three benzene rings. It has, however, been shown by crystal structure studies that one ring is slightly rotated out-of-plane with respect to the other two, so that there is a further lowering of the symmetry. It would, therefore, be possible to observe split bands with the help of a high resolving power instrument. Under these conditions the intensity of the split bands is expected to be very low as has rightly been observed by Deacon and Green¹³ and Steger and Stopperka.¹⁶ In the phosphonium compounds the formal positive charge on the phosphorus atom discussed earlier, creates polarity in the rings by attracting their π -electron density and results in the enhancement of the intensity. Furthermore, the absorption due to the individual rings is also altered which gives rise to frequency shifts and hence better resolution.

This idea of individual ring absorption is further supported by the pattern of the splittings. In the methyltriphenylphosphonium iodide the splitting of

the higher frequency band at 760 cm^{-1} is not well marked and occurs only as a shoulder while in ethyltriphenylphosphonium iodide it is a medium intensity band and in propyltriphenylphosphonium iodide three discrete absorption bands are observed. In the butyltriphenylphosphonium iodide, however, the observed bands are broadened. An increase in the chain-length further increases the polarity, since these groups have a positive inductive effect. This changes the amount of twisting still further providing greater chances of interaction between the rings and the aliphatic chain.

As is very well-known, the structure of the compounds in the crystal may be different from that in the solution. Crystal structure studies confirm the views on the rotation or twisting of the benzene rings in the crystalline state.²⁴ Rose and Mooney²⁵ have suggested that the crystal of the tetraphenylarsonium cation has two reflecting planes at right angles to each other and to the basal plane. In triphenylphosphine¹⁶ one ring is inclined towards the molecular axis by about 30° more than the other two rings. Because of the degeneracy under low resolution only one band is observed in triphenylphosphine while in the phosphonium compounds the band is split into three since all the three rings are in different planes. It is quite likely that in the phosphine also the rings are in different planes and since in the crystalline state the movement is restricted, only a single band is observed, under low resolving conditions.

According to Sheldon and Tyree,¹⁸ a band is observed near 720 cm^{-1} , whenever the phosphine acts as a donor or it is in the 4 coordinated state. This band is sometimes partially or totally split into a doublet. Deacon and Jones have assigned the band at 722 cm^{-1} to the X-sensitive mode *r* whereas Sandorfy²³ suggests it to be due to the CH_2 rocking frequency. This band is very weak in the case of triphenylphosphine and cannot be assigned to the X-sensitive mode *r*, since in that case it is expected to absorb strongly. A comparison of the spectra of $(\text{alkyl})_3\text{P}$, Alkyl_3RPX , shows that the spectra of the alkylphosphonium compounds do not show any band in this region. This band is, therefore, not related to the 4 coordination of phosphorus as pointed out by Sheldon and Tyree and should be assigned to a CH_2 rocking vibration.

A very strong band near 692 cm^{-1} has been assigned to out-of-plane ring deformation mode *v*, while the one at 650 cm^{-1} in phosphine and 670 and 650 cm^{-1} in ethyltriphenylphosphonium compounds is suggested to be due to X-sensitive mode *r*.

650–250 cm^{-1} Region. In this region three X-sensitive modes *y*, *t* and *u* and one out-of-plane ring deformation mode *w* are found to absorb and have the following characteristic features: (1) two weak bands are noted in the spectrum of the phosphine at 625 and 545 cm^{-1} , the same are absent from the phosphonium compounds, (2) the band near $455 \pm 5\text{ cm}^{-1}$ is found only in the phosphonium compounds and shows a gradual shift in frequency with increasing chain-length, and (3) the bands at 515 and 440 cm^{-1} shift towards lower frequencies as the alkyl group becomes more and more bulky.

The two bands observed at 625 and 545 cm^{-1} in the phosphine have also been recorded by various workers. Steger and Stopperka have assigned it to (ω 23) vibrations while Deacon and Green have left it unassigned. For monosubstituted benzenes $\phi(\text{C}-\text{C}-\text{C}-)$ mode s is expected to absorb at 620 cm^{-1} . Hence in the present case it is reasonable to assign it to the same vibration. The absorption at 545 cm^{-1} is absent from the phosphine spectrum and a very strong absorption is found in the phosphonium compounds near 530 cm^{-1} . This band has not been assigned. A very strong band found between 500-515 cm^{-1} in the phosphine and the phosphonium compounds has been assigned by Deacon and Jones¹² as an out-of-plane deformation mode y. It may also be due to the combination of two X-sensitive modes t and x. The vibration due to mode y occurs in monosubstituted benzenes near 460 cm^{-1} . This vibration involves an out-of-plane bending of the substituent. In the phosphine and the phosphonium compounds the rings are attached to a common substituent. For this reason slightly higher frequencies are expected for this mode and hence the band occurring at about 490 cm^{-1} may be assigned to mode y.

A weak to medium intensity band is found at 450 cm^{-1} in all the phenylphosphonium compounds which has not been assigned. Another weak to medium intensity band at 432 cm^{-1} found in phosphine and at 440 cm^{-1} in the ethyl compound shows a slight shift with increasing molecular weight. This absorption has been assigned to the X-sensitive mode t. Deacon and Jones have assigned it to the stretching vibrations. The band at 420 cm^{-1} has been assigned to X-sensitive mode u. This band is split into two peaks in the butyl compound. The out-of-plane ring deformation mode w is found to absorb near 400 cm^{-1} in all the compounds. It has a very high intensity for the propyl compound and is split in the butyl compound.

Alkyltriphenylphosphonium Bromides

The alkyltriphenylphosphonium bromides are recorded in Table 2 which includes intensity data and assignments of various absorptions. It might be seen that excepting the following characteristic features, the bromides have also the same pattern of absorption as the iodides: (1) the intensities are enhanced three times in the bromide compounds compared with the corresponding iodides, (2) slight shifts are observed for some band positions, and (3) more split bands are found to occur for the bromides than the iodides.

The above features of absorption show the participation of the anion in the overall vibrational pattern of the molecules. Thus the enhancement in the intensity in the present case may be related to the higher electronegativity of the bromide which increases the positive charge on the central atom. This creates greater polarizability in the rings and hence the enhancement in the intensity. The same reason should also apply to the shift in the frequency to

shorter wavelengths for certain vibrations. Mode o for example is shifted to 1330 cm^{-1} from the usual position at 1320 \pm 5 cm^{-1} in the phosphine and phosphonium iodides, and mode m to 1470 cm^{-1} from 1485 cm^{-1} . It is interesting to note that the band at 780 \pm 10 due to P—C stretching vibrations in the phosphonium iodides is shifted to lower frequencies in the bromides and now occurs at 765 \pm 5 cm^{-1} . This shift also suggests the participation of the anion in the overall pattern of absorption. Here the increase in the positive charges results in a lowering of the P—C bond order.

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